Dynamic response of ultrathin highly dense ZIF-8 nanofilms

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Materials and Reagents

Commercial reagents were purchased from Sigma-Aldrich (A.C.S. grade) and used without any further purification. Single side polished silicon wafers, comprising *ca*. 2 nm native oxide layer, were obtained from the Mesa+ Institute for Nanotechnology.

Synthesis of the initial solutions

A metal precursor solution was prepared by dissolving 1.5 g of zinc chloride ($ZnCl_2$) in 40 ml of methanol. The organic linker solution was synthesized by dissolving 2.5 g of 2-methylimidazole ($C_4H_5N_2$) in methanol. Both solutions were vigorously stirred for 30 minutes under ambient conditions, capped and put aside for 24 hours to reach equilibrium.

Synthesis of ZIF-8 nanofilms

The experiments were performed at room temperature under ambient atmospheric conditions. Silicon wafers were vertically immersed into the zinc solution for 30 minutes. After immersion in the zinc solution, the samples were washed with methanol and dipped into the ligand solution for 30 minutes, followed by final solvent washing. The withdrawal speed for each step was kept constant. Each set of experiments was performed utilizing withdrawal speeds ranging between 0.1 - 4 mm s^{-1}. As-synthesized films were placed under a petri dish and dried at ambient conditions over 2 days.

Structural characterization

Long distance Scanning Electron Microscopy (SEM) micrographs were obtained using a JEOL JSM-6010LA (JEOL Ltd.) operated at 5 keV acceleration, whilst in-depth analysis was performed on a JEOL JSM-6000F (JEOL Ltd.) SEM under 10 - 15 keV. Prior to SEM analysis, samples were coated with an Au layer to mitigate charging. X-ray diffraction (XRD) studies were performed at room temperature on a X'Pert PRO θ-θ powder diffractometer (PANanalytical) with parafocusing Bragg-Brentano geometry using Cu-Kα radiation (λ = 1.5418 Å, U = 40 kV, I = 30 mA). The data were scanned with an ultrafast detector X'Celerator over the angular range 5-30º

(2θ) with a step size of 0.0688º (2θ) and a counting time of 406.4 s step^{-1}. XRD data evaluation was performed using HighScore Plus software.

Ellipsometry measurements

Ex situ ellipsometry measurements were conducted on a variable angle spectroscopic ellipsometer (M-2000X; J.A. Woollam Co., Inc.) operating in a maximum wavelength range of 210-1000 nm. The angles of incidence of the probing light beam were 65, 70 and 75°, with the spot size of *ca*. 2 mm. CO_2 sorption measurements were performed on spectroscopic ellipsometer (Alpha-SE; J. A. Woollam Co., Inc.) coupled with a custom-built high-pressure stainless steel cell (1 cm thick transparent windows). The spectral range was 380-900 nm. The measurements involved real time *in situ* monitoring of the refractive index and the film thickness upon variation of the CO_2 partial pressure (0.2 – 1 bar) controlled with a syringe pump (ISCO 500D; Teledyne). The sample was de-gassed prior to the sorption measurements. The cell temperature was kept constant at 35 °C. Experiments were performed in a dynamic mode with 30 seconds per full spectral scan.

For the sorption measurements, ZIF-8 film synthesized at $u > u_c$ was selected due to the greater thickness allowing for high-fidelity deconvolution of thickness and refractive index in the ellipsometry data analysis. For thinner films these parameters may be correlated. Even though thicker, the films are consider to have a very similar morphology as the one obtained at u_c, due to the similar refractive indices.

The spectroscopic data analysis was performed with the CompleteEASE software (Woollam Co., Inc.). The thicknesses of the films were obtained from the spectroscopic ellipsometry measurements, employing the Cauchy model of optical dispersion in the spectral region of 340-1000 nm and 380-900 nm for the M-2000X and Alpha-SE, respectively. For the M-2000X the spectral range from 210-340 nm was omitted due to a slight light depolarization by the sample. The ~2 nm native oxide layer was accounted for and incorporated into the optical model. The optical model included the pressure-dependent refractive index of the compressed CO_2 gas, as well as the slight birefringence effects induced by mechanical strains in the windows.

Estimation of ZIF-8 film porosity

The porosity of the ZIF-8 films was determined from the film's refractive index using the Bruggeman Effective Medium Approximation (EMA) theory [1]. The fresh film prepared at 4 mm s^{-1} withdrawal speed (n_{fresh} = 1.5495; Manuscript, Fig. 1c) is assumed to comprise a mixture of the ZIF-8 matrix ($n_{ZIF\text{-}8}$) and liquid methanol (n_{MeOH} = 1.325 [2]). The volume fractions of the components are $\Phi_{ZIF\text{-}8}$ and Φ_{MeOH} respectively, and since these are the only two components $\Phi_{MeOH} = 1 - \Phi_{ZIF\text{-}8}$. For this system EMA can be written as follows:

$$\frac{n_{ZIF-8}^2 - n_{fresh}^2}{n_{ZIF-8}^2 + 2n_{fresh}^2} \cdot \phi_{ZIF-8} + \frac{n_{MeOH}^2 - n_{fresh}^2}{n_{MeOH}^2 + 2n_{fresh}^2} \cdot (1 - \phi_{ZIF-8}) = 0 \qquad \text{eq. 1}$$

After exposure of the same sample to vacuum and helium flow (Manuscript, Fig. 3) it is assumed that all of methanol is removed and the treated sample consist of the ZIF-8 matrix ($n_{\text{ZIF-8}}$) and void ($n_{\text{void}} = 1$). The value for the refractive index of the treated sample is taken directly before the exposure to CO_2/He mixtures, $n_{\text{treated}} = 1.4256$. The volume fraction of void (Φ_{void}) is assumed to be equal to the void fraction of methanol in the fresh film: $\Phi_{\text{void}} = \Phi_{\text{MeOH}} = 1 - \Phi_{\text{ZIF-8}}$. The EMA written for the treated sample:

$$\frac{n_{ZIF-8}^2 - n_{treated}^2}{n_{ZIF-8}^2 + 2n_{treated}^2} \cdot \phi_{ZIF-8} + \frac{n_{void}^2 - n_{treated}^2}{n_{void}^2 + 2n_{treated}^2} \cdot (1 - \phi_{ZIF-8}) = 0 \qquad \text{eq. 2}$$

Solving this set of equations yields: $n_{\text{ZIF-8}} = 1.6805$ and $\Phi_{\text{ZIF-8}} = 0.64$. The porosity can be calculated as $\Phi_{\text{void}} = 1 - \Phi_{\text{ZIF-8}} = 0.36$.

XRD pattern of ZIF-8 nanofilm for one and two deposition cycles

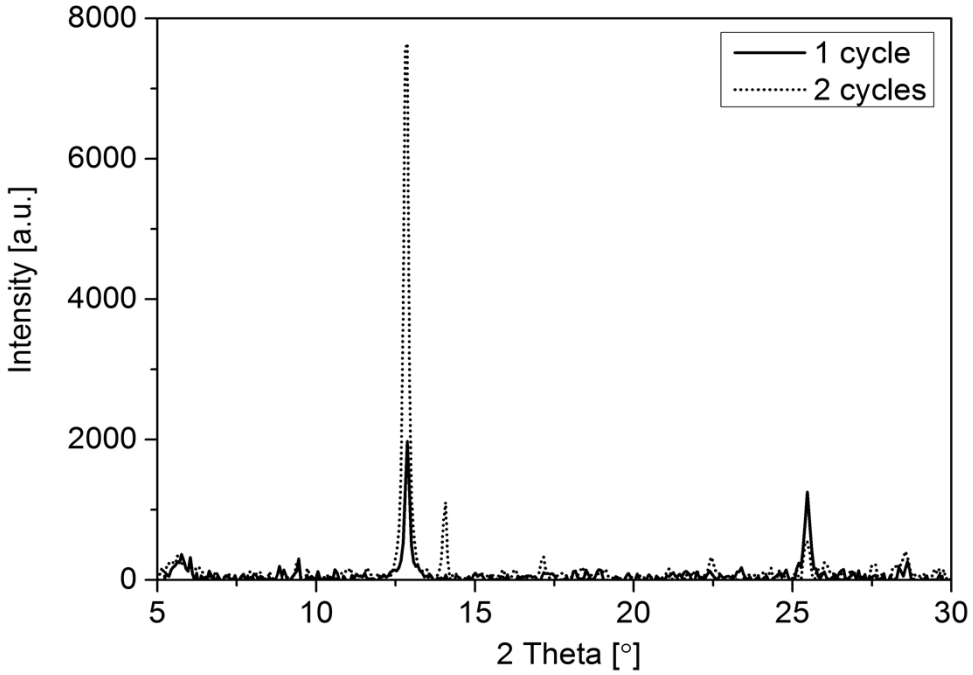

Fig. S1 X-Ray Diffraction pattern for 1 (solid line) and 2 (dotted line) deposition cycles. The repetition of a deposition cycle results in the formation of larger crystals manifesting in greater peak intensity.

CO_2 concentration as a result of increased gas partial pressure

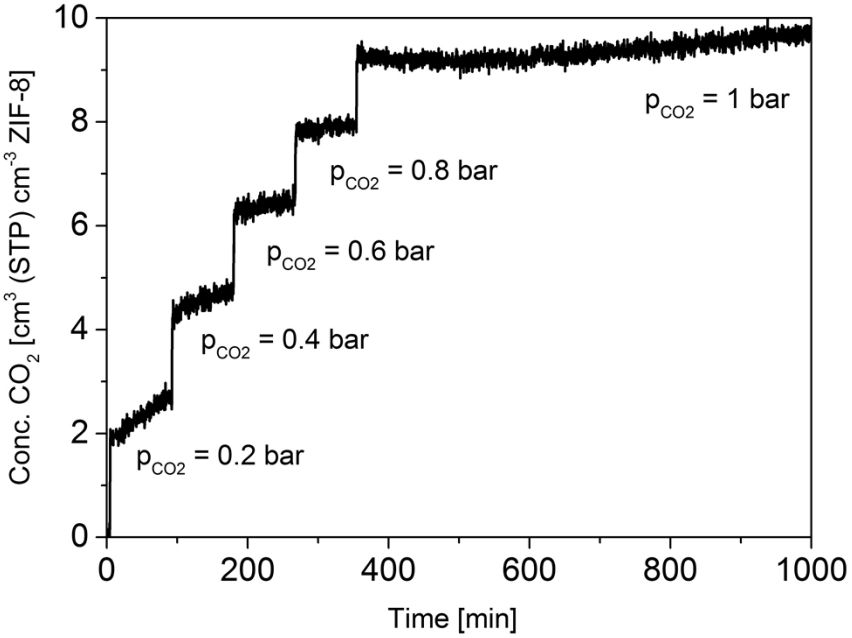

Fig. S2 Carbon dioxide sorption in ZIF-8 nanofilm (u = 4 mm s^{-1}) as a response to stepwise introduction of CO_2. Each step represents additional 0.2 bar increase in CO_2 partial pressure.

Dynamic response of one year aged ZIF-8 nanofilm

For the estimation of film longevity, the sample was left under the ambient conditions for a period of one year. The refractive index and the film thickness, determined from three spots measurements on a film developed at u = 4 mm s^{-1}, show a decrease of *ca*. 15 nm and <1% in the film thickness and the refractive index, respectively, as compared to the values obtained at the end of CO_2 sorption experiment (h = 181.7 nm, n = 1.528). These changes are likely to be attributed to the morphological transformation of non-equilibrium phase of the film over extended time period. However, the response of the one year aged nanofilm to pure CO_2 was found consistent with the freshly-synthesized films. Precisely, when exposed to pure CO_2, the refractive index increments were Δn = 0.0054 (0.37% increase) and Δn = 0.0043 (0.3% increase) for as-synthesized and one year aged film, respectively (Fig S3).

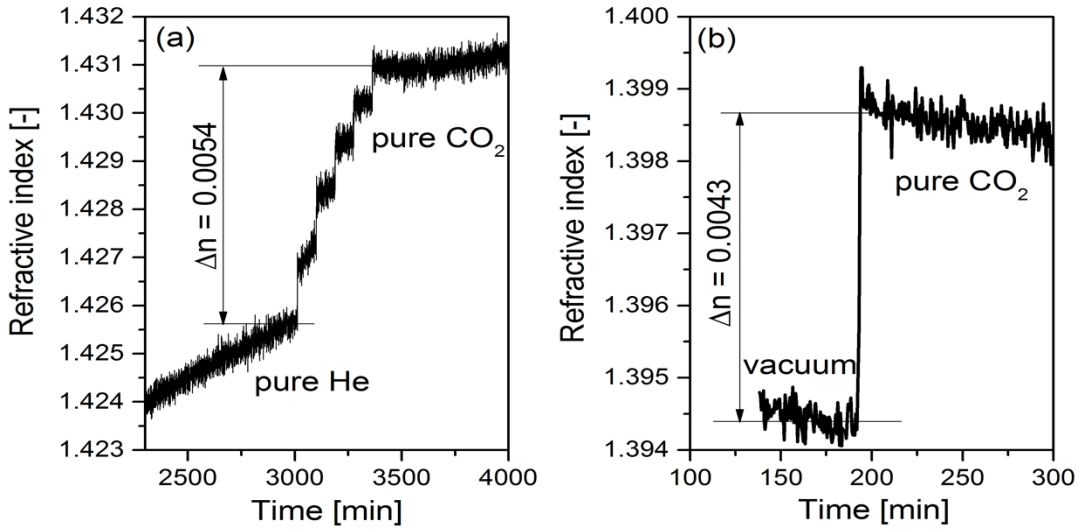

Fig. S3 Response of freshly-synthesized (a) and one year-aged (b) ZIF-8 nanofilm to pure CO_2. Film synthesized at u = 4 mm s^{-1}.

Acknowledgments

We gratefully acknowledge the financial support from Erasmus Mundus Doctorate in Membrane Engineering (EUDIME; ref. No. 511944-1-2010-1-IT-EMJD).

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